Renewable and Sustainable Energy Reviews 16 (2012) 4406–4414

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Bio-oil production and upgrading research: A review

Shuangning Xiu*, Abolghasem Shahbazi

Biological Engineering Program, Department of Natural Resource and Environmental Design, North Carolina A&T State University, 1601 E.Market Street, Greensboro, NC 27410, U.S.A

ARTICLE INFO

Article history:
Received 8 September 2011
Received in revised form
11 April 2012
Accepted 18 April 2012
Available online 20 June 2012

Keywords:
Bio-oil
Biomass
Pyrolysis
Upgrading
Hydrothermal liquefaction

ABSTRACT

Biomass can be utilized to produce bio-oil, a promising alternative energy source for the limited crude oil. There are mainly two processes involved in the conversion of biomass to bio-oil: flash pyrolysis and hydrothermal liquefaction. The cost of bio-oil production from biomass is relatively high based on current technologies, and the main challenges are the low yield and poor bio-oil quality. Considerable research efforts have been made to improve the bio-oil production from biomass. Scientific and technical developments towards improving bio-oil yield and quality to date are reviewed, with an emphasis on bio-oil upgrading research. Furthermore, the article covers some major issues that associated with bio-oil from biomass, which includes bio-oil basics (e.g., characteristics, chemistry), application, environmental and economic assessment. It also points out barriers to achieving improvements in the future.

Contents

1. Introduction

Ever since the shortages of petroleum resources began with the global energy crisis in the 1970s, considerable attention has been focused on the development of alternative fuels. Renewable biomass sources can be converted to fuels and are a logical choice to replace oil. Unlike fossil fuel, biomass takes carbon out of the atmosphere while it is growing, and returns it as it is burned. This maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels.

All biomass is produced by green plants converting sunlight into plant material through photosynthesis. Biomass fuels potential include wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous crops, animal wastes, and a

* Corresponding author. Tel.: +1 3363347787; fax: +1 3363347270.
E-mail address: xshuangn@ncat.edu (S. Xiu).

1364-0321/$ - see front matter
http://dx.doi.org/10.1016/j.rser.2012.04.028

host of other materials [1]. Biomass can be converted to various forms of energy by numerous technical processes, depending on the raw material characteristics and the type of energy desired. As a result, a wide variety of conversion schemes have been developed. Among various conversion technologies, thermochemical conversion (e.g., pyrolysis, hydrothermal liquefaction) of biomass offers a convenient way to produce liquid fuels. The liquid products, known as bio-oils, have been regarded as promising candidates to replace petroleum fuels for power generation, heat, or for extraction of valuable chemicals.

Biomass can be converted to bio-oil by two main routes: flash pyrolysis and hydrothermal liquefaction (HTL). Flash pyrolysis involves the rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquids, gases, and char. HTL involves the reaction of biomass in water at elevated temperature and pressure with or without the presence of a catalyst [2]. The former requires a relatively dry biomass but the latter is tolerant to high moisture content and so is ideally suited to biomass from an aquatic origin. During the past decade considerable efforts have been devoted to the development of pyrolysis techniques for the production of bio-oil [3,4]. Unlike flash pyrolysis, technological developments in the area of HTL are at an early developmental stage. Only limited information so far is available on the systematic study of HTL including process development, mechanism study and bio-oil application, etc.

Bio-oil has several environmental advantages over fossil fuels as a clean fuel. Bio-oils are CO_2/GHG neutral. Therefore, they can generate carbon dioxide credits. No SO*x* emissions are generated, because plant biomass contains insignificant amounts of sulfur. Therefore, bio-oil would not be subjected to SO*x* taxes. Bio-oil fuels generate more than 50% lower NO*x* emissions than diesel oil in a gas turbine. Renewable and locally produced bio-oil can be produced in countries with large volumes of organic wastes. Thus, bio-oils are cleaner and cause less pollution. However, the potential of for direct substitution of bio-oil for petroleum fuels and chemical feedstocks is limited due to their high viscosity, high water and ash contents, low heating value, instability and high corrosiveness. Consequently, upgrading of bio-oil is necessary to give a liquid product that can be used as a liquid fuel or chemical feedstocks in various applications.

This article comprehensively reviews the state of the art, the use and drawbacks of the processes that are used to produce and upgrade bio-oil, with an emphasis on hydrothermal liquefaction process. Besides, some major issues that associated with oil from biomass, which includes oil evaluation and composition (e.g., characteristics, chemistry), application, environmental and economic assessment are also discussed in this article. It also points out challenges to success with bio-oils in the future.

2. Bio-oil production from biomass

2.1. Current processes for conversion of biomass to bio-oils

Two main types of processes for production of bio-oils from biomass are flash pyrolysis and hydrothermal liquefaction (HTL). Flash pyrolysis involves the rapid thermal decomposition of organic compounds by heat in the absence of oxygen, which results in the production of charcoal, bio-oil, and gaseous products. HTL is also called direct liquefaction, hydrothermal upgrading/pyrolysis, depolymerization, and solvolysis, which is conducted under elevated pressure and temperature to keep water in either liquid or supercritical state. The use of water as a solvent obviates the need to dry biomass and permits reactions to be carried out at lower temperatures in comparison with flash pyrolysis. The primary product of HTL is bio-oil or bio-crude, and the main byproducts are the solid residue, bio-char, and water containing soluble organic compounds. Both of the processes belong to the thermochemical technologies in which feedstock organic compounds are converted into bio-oil products. An advantage of the thermochemical process is that it is relatively simple, usually requiring only one reactor, thus having a low capital cost. However, this process is non-selective, producing a wide range of products including a large amount of char [5].

The characteristic and technique feasibility of the two thermochemical processes for bio-oil production are compared in Table 1. Flash pyrolysis is characterized by a short gas residence time (~1 s), atmospheric pressure, and a relatively high temperature (450–500 °C). Furthermore, feedstock drying is necessary. Hydrothermal liquefaction is usually performed at lower temperatures (300–400 °C), longer residence times (0.2–1.0 h.), and relatively high operating pressure (5–20 Mpa). Contrary to flash pyrolysis and gasification processes, drying the feedstock is not needed in the HTL process, which makes it especially suitable for naturally wet biomass. However, a reducing gas and/or a catalyst are often included in the process in order to increase the oil yield and quality.

The reaction mechanisms of the two processes are different, which have been studied by many investigators [6,7]. The hydrothermal process occurred in aqueous medium which involves complex sequences of reactions including solvolysis, dehydration, decarboxylation, and hydrogenation of functional groups, etc. [8]. The decomposition of cellulose was studied by Minowa et al. [9]. The effects of adding a sodium carbonate catalyst, a reduced nickel catalyst, and no catalyst addition in the decomposition of cellulose in hot-compressed water were investigated. They found that hydrolysis can play an important role in forming glucose/oligomer, which can quickly decompose into non-glucose aqueous products, oil, char and gases (Fig. 1). Without a catalyst, char and gases were produced through oil as intermediates. However,

Table 1
Comparison of two typical thermochemical processes for bio-oil production.

Methods	Treatment condition/requirement	Reaction mechanism/process description	Technique feasibility	
			Pros.	Cons.
Flash/fast pyrolysis	Relatively high temperature (450–500 °C); a short residence time (~1 s); atmosphere pressure; drying necessary	The light small molecules are converted to oily products through homogeneous reactions in the gas phase	High oil yield up to 80% on dry feed; lower capital cost; Commercialized already	Poor fuel quality obtained
Hydrothermal liquefaction (HTL)/ liquefaction/ hydrothermal pyrolysis	Lower temperature (300–400 °C); longer residence time (0.2–1.0 h.); high pressure (5–20 Mpa); drying unnecessary	Occurs in aqueous medium which involves complex sequences of reactions	Better quality of bio-oil obtained (high heating value, low moisture content)	Relatively low oil yield (20–60%); need high pressure equip, thus higher capital cost

in the presence of an alkali catalyst, char production was inhibited because the oil intermediates were stabilized, resulting in oil production. Reduced nickel was found to catalyze the steam reforming reaction of aqueous products as intermediates and the machination reaction. Typical yields of liquid products for hydrothermal conversion processes were in the range of 7–70%, depending on many factors including substrate type, temperature, pressure, residence time, type of solvents, and catalysts employed [10].

With flash pyrolysis, the light small molecules are converted to oily products through homogeneous reactions in the gas phase. A number of pyrolysis mechanisms have been proposed, such as widely used Broido–Shafizadeh model [11]. A comprehensive review of the myriad models available for describing the biomass pyrolysis reactions is beyond the scope of this communication. However, those models have been thoroughly reviewed by other researchers [12,13]. For example, Blasi et al. has thoroughly reviewed many semi-global mechanisms that have been proposed in the literature and compared them in the terms of weight low kinetics and species selectivity [12].The relatively simple single particle pyrolysis model is shown in Fig.2. Biomass is rapidly heated in the absence of air, vaporizes, and quickly condenses to bio-oil. The main product, bio-oil, is obtained in yields of up to 80 wt% on dry feed, together with the by-product char and gas [3].

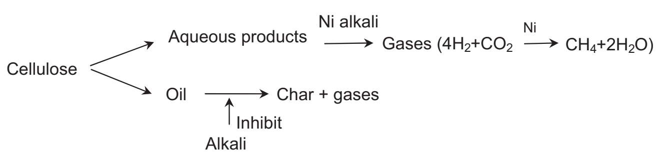


Fig. 1. Reaction pathway for the hydrothermal liquefaction of cellulose.

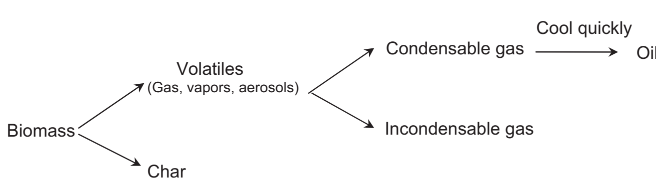


Fig. 2. Reaction pathway for the biomass flash pyrolysis process.

2.2. *Research development of flash pyrolysis and hydrothermal liquefaction*

Flash pyrolysis for the production of liquids has developed considerably since the first experiments in the late 1970s. Several pyrolysis reactors and processes have been investigated and developed to the point where fast pyrolysis is now an accepted, feasible and viable route to renewable liquid fuels, chemicals and derived products. Since the 1990s, several research organizations have successfully established large-scale fast pyrolysis plants. Bridgwater and Peacocke [3] have intensively reviewed the key features of fast pyrolysis and the resultant liquid product, and described the major reaction systems and processes that have been developed over the last 20 years.

Recently, Venderbosch and Prins [4] reviewed fast pyrolysis technologies, and concluded that challenges for the coming years are (1) improvement of the reliability of pyrolysis reactors and processes; (2) the demonstration of the oil's utilization in boilers, engines and turbines; and (3) the development of technologies for the production of chemicals and biofuels from pyrolysis oils.

Unlike flash pyrolysis, technological developments in the area of HTL present new ways to turn wastes to fuel. HTL was initially developed for turning coal into liquid fuels, but recently, the technique has been applied to a number of feedstocks, including woody biomass, agricultural residues, organic wastes (e.g., animal wastes, sewage sludge), and aquatic plants. Table 2 summarizes representative literature data of hydrothermal liquefaction of common types of biomass and the most influential operating parameters. As can be seen from Table 2, organic waste materials are more favorable than woody biomass and agricultural residues for HTL process, owing to their higher oil yield and the higher heating value of their bio-oil products. This earlier work was very promising, showing that HTL can be used as an efficient method to treat different types of biomass and produce a liquid biofuel. In particular, HTL technology present a unique approach to mitigate the environmental and economic problems related to disposing of large volumes of organic wastes. It not only reduces the pollutants, but also produces useful energy in the form of liquid fuel.

Compared with flash pyrolysis, HTL is at an early developmental stage, and the reaction mechanisms and kinetics are not yet fully understood. Mostly, the approach is to carry out HTL experiments for selected types of biomass and analyze the processing conditions on the oil yield and quality of the products. The processing conditions include final liquefaction temperature,

Table 2
Overview of literature on hydrothermal liquefaction of common types of biomass.

Raw materials	Reactor capacity	Temp. (°C)	Pressure (Mpa)	Time (min)	Oil Yield[a](wt%/VS)	Heating value (MJ/kg)	Reference
a) Woods							
Beech	–	277–377	–	25	16.8–28.4%	27.6–31.3	[15]
Spruce	–	277–377	–	25	13.8–25.8%	28.3–33.9	[15]
Pine Sawdust	0.2 L	280	–	15	7.2–11.3%	–	[19]
b) Agricultural residues							
Corn stalk	0.3 L	300	10	30	28.3%/VS	29.7	[9]
Rice husk	0.3 L	300	10	30	28.8%/VS	30.8	[9]
Rice straw	1.0 L	260–350	6–18	3–5	13.0–38.35%	27.6–35.8	[20]
c) Organic wastes							
Swine manure	1 L autoclave	260–340	5–17.8	0–90	14.9–24.2%	36.1	[21]
Swine manure	Continuous mode	285–305	9–12	40–80	35–70%/VS	25.2–33.1	[22]
Cattle manure	1.8 L autoclave	270–350			27.97–48.78%/VS	35.5	[23]
Sewage sludge	20 kg/h.	300–360	10–18	5–20	–	30–35	[24]
d) Aquatic plants							
Duckweed	1 L autoclave	250–374	4.1–22.1	5–90	10–30.3%	33.95	[25]
Algae	2 L autoclave	200–300	8.9–10.3	30–120	24–39.4%	21.3–38.5	[26]

[a] Note: For some references, bio-oil yield is calculated based on volatile solids (VS) of initial input biomass.

residence times, rate of biomass heating, size of biomass particles, type of solvent media and hydrogen donor solvents. The yield and quality of the bio-oil is significantly affected by the operating parameters. Scattered information about processing parameters has been discussed in original articles, technical notes, and review papers. Until recently, Akhtar and Amin [14] presented a systematic overview of the effect of these parameters on the yield and composition of the liquid products. In general, most R&D work has been focus on maximizing the overall oil yield, without paying sufficiently attention to the interaction of these parameters as well as their effect on the product composition and quality.

Biomass is a very heterogeneous and chemically complex renewable resource. Bio-oil production from HTL is affected by the type of biomass due to their different chemical compositions and physical structures [9]. Various types of biomass have been used as feedstocks for HTL process, as illustrated in Table 2. Though extremely relevant for both the oil yield and oil quality, limited research has been carried out to understand the effects of individual compounds and their interactions (e.g., ash, proteins) on the HTL reactions. Cellulose, lignin and hemicelluloses have been used as individual model compounds to study the reaction pathways and decomposition mechanism [15–17]. It found that presence of high amount of lignin contents leads to the formation of char residue. Hemicelluloses and cellulose are favorable for the bio-oil yield [14]. However, wastes materials are more complex in terms of composition. It's believe that any organic material, specifically carbohydrates, proteins, and fats could be converted into crude oil [9,18]. Until now, results of laboratory investigations are quite poor regarding the understanding of what is actually taking place and how the compositions of biomass affect the process. Thus, a rigorous study involving the use of combinations of different model compounds (carbohydrates, proteins, fats, mineral content and ash) to simulate a wide variety of waste feedstock may prove more useful.

Studies on HTL were predominately conducted in batch scale (Table 2). However, some researchers also investigated the HTL process in continuous systems. Chornet and overend [8] compiled a list of available information on continuous biomass HTL process. Itoh et al. [27] developed a scale-up of hydrothermal liquefaction of sewage sludge to produce oils. The demonstration plant with a capacity of 5 t/day was operated at a temperature of 300 °C and 10 Mpa. In 2005, University of Illinois at Urbana-Champaign developed a small-scale continuous hydrothermal process reactor system [22] and converted fresh swine manure into bio-oil. It had a capacity to process up to 48 kg of manure slurry per day. Worldwide Bioenergy, LLC has commercialized this technology and built a pilot plant with a capacity of 40 barrels/day in Houston, Texas. Although the operation of the early designed reactor showed satisfactory results, the design was not free of problems. Slurry feeding was problematic due to the high-pressure pump durability issues. In summary, none of the research organizations or commercial entities has succeeded to a point where they have developed standardized systems that are purchased based on economics. Furthermore, the reliability of these commercialized systems remains unknown.

3. Bio-oil

3.1. Properties of bio-oils

Bio-oils are usually dark brown, free-flowing liquids having a distinctive smoky odor. The physical properties of bio-oils are described in several publications [14,28]. The different physical properties of bio-oils result from the chemical composition of the oils, which is significantly different from that of petroleum-derived oils. Bio-oil is a complex mixture of several hundreds of organic compounds, mainly including acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers. Some of these compounds are directly related to the undesirable properties of bio-oil. Basic data for liquefied bio-oils from swine manure, pyrolysis bio-oil from wood and conventional petroleum fuels are compared in Table 3.

As shown in Table 3, liquefied oils have much lower oxygen and moisture contents, and consequently much higher energy value, as compared to oils from fast pyrolysis. The corresponding HHV of liquefied oil from swine manure is 36.05 MJ/kg, which about 90% of that of heavy fuel oil (40 MJ/kg). The properties of bio-oil from both processes are significantly different from heavy petroleum fuel oil. Compared with heavy petroleum fuel oil, the bio-oils have the following undesired properties for fuel applications:

(1) high water content
(2) high viscosity
(3) high ash content
(4) high oxygen content (low heating value)
(5) high corrosiveness (acidity)

These undesired properties have so far limited the range of bio-oil application. The differences in processing conditions and feedstock result in significant differences in the product yield and product composition of bio-oils. Recently, Lu et al. [28] intensively reviewed the fuel properties of fast pyrolysis oils and discussed how these properties affect the utilization of bio-oils.

Table 3
Comparison of selected properties of bio-oils produced by hydrothermal liquefaction of swine manure and pyrolysis of wood and heavy fuel oil.

Properties		Liquefied bio-oil from swine manure [21]	Pyrolysis bio-oil from wood [39]	Heavy petroleum fuel oil [40]
Moisture content (wt%)		2.37	15–30	0.1
pH		–	2.5	–
Specific gravity		1	1.2	0.94
Elemental composition (wt%)	C	72.58	54–58	85
	H	9.76	5.5–7.0	11
	O	13.19	35–40	1.0
	N	4.47	0–0.2	0.3
Ash		0.78	0–0.2	0.1
HHV(MJ/kg)		36.05	16–19	40
Viscosity(at 50 °C)(cP)		843	40–100	180
Solids (wt%)		–	0.2–1	1
Distillation residue (wt%)		63	Up to 50	1

Overall, bio-oils cannot be directly used as transportation fuels due to their high viscosity, high water and ash contents, low heating value, instability and high corrosiveness. Therefore, upgrading of bio-oil is needed to improve its properties for liquid fuel.

3.2. Uses of bio-oils

As a renewable liquid fuel, bio-oil can be readily stored and transported. It can serve as a substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines, and turbines for electricity generation. Alternatively, the crude oil could serve as a raw material for the production of adhesives, phenol-formaldehyde-type resins, wood flavors, etc. Different specialty chemicals form the bio-oils are also possible after further processing and separation. The following are some industrial uses of bio-oil:

(1) Combustion fuel in boiler/burner/furnace systems for heat generation[29],
(2) Combustion in diesel engines/turbines for power generation [30,31],
(3) Can be used as a transportation fuel after upgrading [32,33],
(4) Production of anhydro-sugars like levoglucosan, which has potential for the manufacturing of pharmaceuticals, surfactants, biodegradable polymers [34],
(5) Can be used as liquid smoke and wood flavors [35],
(6) Production of chemicals and resins (e.g., agri-chemicals, fertilizers, acids and emission control agents) [36,37],
(7) Can be used in making adhesives, e.g., asphalt bio-binder [38].

4. Upgrading of bio-oil

Considering the above discussion on the properties of bio-oils, it is obvious that the fuel quality of bio-oils is inferior to that of petroleum-based fuels. There have been intensive studies on bio-oil upgrading research and various technologies have been developed for bio-oil upgrading. Table 4 summarizes current techniques used for bio-oil upgrading. The characteristics, as well as recent progress, advantages, and disadvantages of each technique are also described below.

4.1. Hydrotreating

It is generally recognized that the higher the hydrogen content of a petroleum product, especially the fuel products, the better the quality. This knowledge has stimulated the use of a hydrogen-adding process in the refinery, which is called hydrogenation. Currently, the most widely used hydrogenation processes for the conversion of petroleum and petroleum products is hydrotreating. Hydrotreating (HDT) is a nondestructive, or simple hydrogenation process that is used for the purpose of improving product quality without appreciable alteration of the boiling range. Hydrogenation without simultaneous cracking is used for saturating olefins or for converting aromatics to naphthenes. Under atmospheric pressure, olefins can be hydrogenated up to about 500 °C, but beyond this temperature hydrogenation commences. It has become the most common process in modern petroleum refineries. Bio-crude may also be processed by a conventional refinery and potentially augmented with petroleum crude. The oxygen in bio-oils can be removed via hydrotreating. The catalysts commonly used for hydrotreating are sulphide $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ systems [41].

Table 4
Brief description, treatment condition, and technical feasibility of the current techniques used for upgrading bio-oil.

Upgrading methods	Treatment condition/ requirement	Reaction mechanism/process description	Technique feasibility	
			Pros.	Cons.
Hydrotreating/ hydrofining	Mild conditions (~500 °C/low pressure), chemical needed: H_2/CO, catalyst (e.g., CoMo, HDS, NiMo, HZSM-5)	Hydrogenation without simultaneous cracking (eliminating N, O and S as NH_3, H_2O and H_2S)	Cheaper route, commercialized already	High coking (8–25%) and poor quality of fuels obtained
Hydro-cracking/ hydrogenolysis/ catalytic cracking	Severe conditions (>350 °C, 100–2000 Psi), chemical needed: H_2/CO or H_2 donor solvents, catalyst (e.g., Ni/Al_2O_3-TiO_2)	Hydrogenation with simultaneous cracking	Makes large quantities of light products	Need complicated equipment, excess cost, catalyst deactivation, reactor clogging
		Destructive(resulting in low molecular product)		
Sub- /super-critical fluid	Mild conditions, organic solvents needed such as alcohol, acetone, ethyl acetate, glycerol	Promotes the reaction by its unique transport properties: gas-like diffusivity and liquid-like density, thus dissolved materials not soluble in either liquid or gaseous phase of solvent	Higher oil yield, better fuel quality (lower oxygen content, lower viscosity)	Solvent is expensive
Solvent addition(direct add solvent or esterification of the oil with alcohol and acid catalysts)	Mild conditions, polar solvents needed such as water, methanol, ethanol, and furfural	Reduces oil viscosity by three mechanisms: (1) physical dilution (2) molecular dilution or by changing the oil microstructure; (3) chemical reactions like esterification and acetalization	The most practical approach (simplicity, the low cost of some solvents and their beneficial effects on the oil properties)	Mechanisms involved in adding solvent are not quite understand yet
Emulsification/ emulsions	Mild conditions, need surfactant (e.g., CANMET)	Combines with diesel directly. Bio-oil is miscible with diesel fuels with the aid of surfactants	Simple, less corrosive	Requires high energy for production
Steam reforming	High temperature(800–900 °C), need catalyst (e.g., Ni)	Catalytic steam reforming + water–gas shift	Produces H_2 as a clean energy resource	Complicated, requires steady, dependable, fully developed reactors
Chemical extracted from the bio-oils	Mild conditions	Solvent extraction, distillation, or chemical modification	Extract valuable chemicals	Low cost separation and refining techniques still needed

Hydrotreating requires mild conditions, while the yield of bio-oil is relatively low. The process also produces a large amount of char, coke, and tar, which will result in catalyst deactivation and reactor clogging.

4.2. Hydro-cracking

Hydro-cracking is less popular than the hydrotreating in the petroleum industry. Hydro-cracking is a thermal process (> 350 °C) in which hydrogenation accompanies cracking. Relatively high pressure (100 to 2000 psi) is employed, and the overall result is usually a change in the character or quality of the end products [42]. The wide range of products possible from hydro-cracking is the results of combining catalytic cracking reactions with hydrogenation and the multiplicity of reactions that can occur. This process is performed by dual-function catalysts, in which silica–alumina (or zeolite) catalysts provide the cracking function, and platinum and tungsten oxide catalyze the reactions, or nickel provides the hydrogenation function. Alumina is by far the most widely used support.

Hydro-cracking is an effective way to make a large amount of light product, but it requires more severe conditions such as higher temperature and hydrogen pressure to deal with acids, which is not economical and energy efficient.

4.3. Supercritical fluids (SCFs)

A fluid is considered supercritical when its temperature and pressure go above its critical point. SCFs possess unique transport properties. They can effuse through solids like a gas and dissolve materials like a liquid. In particular, SCFs have the ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence to promote the gasification/liquefaction reactions [10]. SCFs have been recently used to improve oil yield and quality and have demonstrated a great potential for producing bio-oil or bio-crude with much higher caloric values and lower viscosity. Water is the cheapest and most commonly used supercritical fluid in hydrothermal processing, but utilizing water as the solvent for liquefaction of biomass has the following drawbacks: (1) lower yields of the water-insoluble oil product; (2) it yields a bio-oil that is very viscous, with a high oxygen content. To enhance the oil yields and qualities, the utilization of organic solvents such as ethanol [10,43], butanol [44], acetone [45,46], 2-propanol [47], *n*-hexanol [45], 1,4-dioxane [48,49], and methanol [50–52] has been adopted. All these solvents have shown a significant effect on bio-oil yield and quality. Minami and Ska [50,51] have reported that 90% of beech wood was successfully decomposed in supercritical methanol. The above motioned supercritical organic solvent fluids are predominately used in HTL process to improve the bio-oil yield and quality. Besides, it was also used to upgrade pyrolysis bio-oil. For example, Tang et al. [53] reported that supercritical ethanol (T=243.1 °C, Pc=6.37 MPa) can upgrade lignin-derived oligomers in pyrolysis oil, and thus reduce the tar or coke.

Although SCFs can be produced at relatively lower temperature and the process is environmentally friendly, these organic solvents are too expensive to make it economically feasible on a large scale. Recently, researchers have been trying to test less expensive organic solvent as a substitute for SCFs. Crude glycerol, the low-value by-product of bio-diesel production, has shown very promising results for being using as a substitute for SCF solvent. Glycerol has been used as an organic solvent for biomass delignification [16,54,55], bio-oil separation [56] and to significantly improve the performance of liquefaction in the conversion of biomass into bio-oil [6,57,58]. Xiu and her colleagues found that bio-oil yield was increased dramatically from 23.9% to 70.92% by use of crude glycerol as a solvent for swine manure HTL process [58]. In addition, they discovered that the free fatty acid in the crude glycerol is the key component that leads to enhancement of the oil yield. Moreover, the oil quality was also improved, having a lower density and viscosity.

4.4. Solvent addition/esterification

Polar solvents such as methanol, ethanol, and furfural have been used for many years to homogenize and to reduce viscosity of biomass oils [59–62]. The immediate effects of adding these polar solvents are decreased viscosity and increased heating value. The increase in heating value for bio-oils mixed with solvents occurs because the solvent has a higher heating value than that of most bio-oils. The solvent addition reduces the oil viscosity due to the following three mechanisms: (1) physical dilution without affecting the chemical reaction rates; (2) reducing the reaction rate by molecular dilution or by changing the oil microstructure; (3) chemical reactions between the solvent and the oil components that prevent further chain growth [40].

Most studies have directly added solvents after pyrolysis, which works well to decrease the viscosity and increase stability and heating value. However, several recent studies showed that reacting the oil with alcohol (e.g., ethanol) and acid catalysts (e.g., acetic acid) at mild conditions by using reactive distillation, resulted in a better bio-oil quality [62–65]. This process is referred to as catalytic esterification or esterification treatment in the literature [66–69].

The chemical reactions that can occur between the bio-oil and methanol or ethanol are esterification and acetalization (Fig. 3). In such a case, the reactive molecules of bio-oil like organic acids and aldehydes are converted by the reactions with alcohols to esters and acetals, respectively. Thus, in addition to the decrease in viscosity and in the aging rate, they also lead to other desirable changes, such as reduced acidity, improved volatility and heating value, and better miscibility with diesel fuels.

Most environmental catalysts applied in bio-oil upgrading are heterogeneous catalysts. Solid acid catalysts, solid base catalysts [70], ionic liquid catalysts [66], HZSM-5, and aluminum silicate catalysts have been investigated for esterification of bio-oils [71,72]. Considering the simplicity, the low cost of some solvents such as methanol and their beneficial effects on the oil, this method seems to be the most practical approach for bio-oil quality upgrading.

4.5. Emulsification (emulsions)

One of the methods in using bio-oil as a combustion fuel in transportation or boilers is to produce an emulsion with other fuel sources. Pyrolysis oils are not miscible with hydrocarbon fuels, but with the aid of surfactants they can be emulsified with

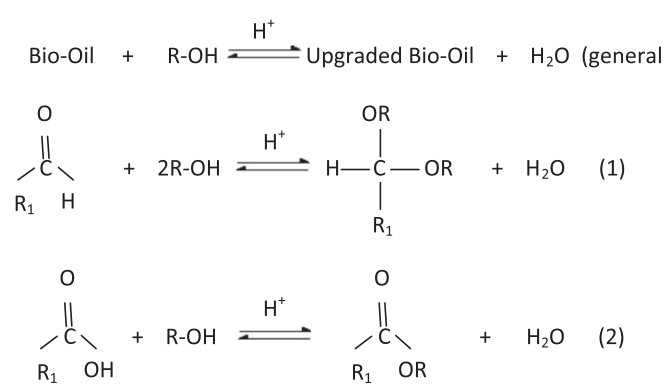


Fig. 3. Reactions involved in bio-oil alcoholysis: (1) acetalization, (2) esterification. [48].

diesel oil. Upgrading of bio-oil through emulsification with diesel oil has been investigated by many researchers [73–77].

A process for producing stable microemulsions, with 5–30% of bio-oil in diesel has been developed at Canmet Energy Technology Centre [40,78]. Those emulsions are less corrosive and show promising ignition characteristics.

Jiang and Ellis [76] investigated the bio-oil emulsification with bio-diesel. A stable bio-oil/bio-diesel emulsion was produced using octanol as an emulsifier. The effects of several process variables on the mixture stability were also examined. They found that the optimal conditions for obtaining a stable mixture between bio-oil and bio-diesel are with an octanol surfactant dosage of 4% by volume, an initial bio-oil/bio-diesel ratio of 4:6 by volume, a stirring intensity of 1200 rpm, a mixing time of 15 min, and an emulsifying temperature of 30 °C. Various properties of the emulsion have shown more desirable values in acid number, viscosity, and water content compared to the original bio-oil. The reduction in viscosity and corrosively of the emulsion was also reported by Ikura et al. [78].

Chiaramonti et al. [74] tested the emulsions from biomass pyrolysis liquid and diesel in engines. Their results suggest that corrosion accelerated by the high velocity turbulent flow in the spray channels is the dominant problem. A stainless steel nozzle has been built and successfully tested. Long-term validation however, is still needed.

More recently, He et al. [79] used a novel high-pressure homogenization (HPH) technique to improve the physicochemical properties and storage stability of switchgrass bio-oil. Compared with the conventional emulsification method, which consists of mixing bio-oil with diesel oil, the HPH technique improved the original properties of bio-oil by decreasing the viscosity and improving its stability in storage. However, the heating value, water content, density, pH value, or ash content did not change.

Overall, upgrading of bio-oil through emulsification with diesel oil is relatively simple. It provides a short-term approach to the use of bio-oil in diesel engines. The emulsions showed promising ignition characteristics, but fuel properties such as heating value, cetane and corrosivity were still unsatisfied. Moreover, this process required high energy for production. Design, production and testing of injectors and fuel pumps made from stainless steel or other materials are required.

4.6. Steam reforming

The term "reforming" was originally used to describe the thermal conversion of petroleum fractions to more volatile products with higher octane numbers, and represented the total effect of many simultaneous reactions such as cracking, dehydrogenation and isomerisation [80]. Reforming also refers to the conversion of hydrocarbon gases and vaporized organic compounds to hydrogen containing gases such as synthesis gas, which is a mixture of carbon monoxide and hydrogen.

Fast pyrolysis of biomass followed by catalytic steam reforming and shift conversion of specific fractions to obtain H_2 from bio-oil was presented as an effective way to upgrade biomass pyrolysis oils. Production of hydrogen from reforming bio-oil was investigated by NREL extensively, including the reactions in a fixed bed and a fluidized bed [81–83]. Commercial nickel catalysts showed good activity in processing biomass derived liquids [84].

4.7. Chemicals extracted from the bio-oils

There are many substances that can be extracted from bio-oil, such as phenols used in the resins industry, volatile organic acids, nitrogen herocycles and *n*-alkanes [2,85]. Most recently, Cao et al. [86] extracted triacetonamine (TAA) in a bio-oil from fast pyrolysis of sewage sludge with a high yield (27.9%) and high purity (80.4%) using acetone as the absorption solvent. Hydrothermal bio-oil contains up to 50 wt% asphalt, which makes it a good candidate for the asphalt industry. Recently, Fini and her colleagues fractionated and chemically modified the bio-oil into an effective alphalt bio-binder, which has remarkable potential to replace or augment petroleum-based road asphalt [38].

The only current commercially important application of bio-oil chemicals is that of wood flavors or liquid smoke [87].Commercialization of special chemicals from bio-oils requires more devotion to developing reliable low cost separation and refining techniques.

5. Conclusions and recommendations for future work

Flash pyrolysis processes are so far the only commercially practiced technology for production of bio-oil or bio-crude from biomass. HTL with a suitable solvent (water or organics) is suitable for high moisture content biomass. In particular, HTL technology present a unique approach to mitigate the environmental and economic problems related to disposing of large volumes of organic wastes. It not only reduces the pollutants, but also produces useful energy in the form of liquid fuel. Compared with flash pyrolysis, HTL is at an early developmental stage, and challenges for the coming years are:

(1) Improvement of oil production rate and energy efficiency of the process. It remains an interesting topic to investigate the interaction of operation parameters on the oil yield and quality during biomass conversion and optimize the process conditions.
(2) Understanding the reaction mechanisms and kinetics. It is important to learn more about the mechanisms involved in the HTL process in order to achieve a desirable oil yield and quality. Because there is a wide range of feedstock that could be used, a systemic approach in determining the effects of various feedstock components to oil yield and quality is needed.
(3) Development of pilot-scale plant. For the up-scale, a detailed economic feasibility study is needed in order to assess the profitability of the process.
(4) The development of technologies for the production of chemicals and biofuels from liquefied oils.

Bio-oils is a promising renewable energy source which have received extensive recognition around the world for their characteristics as combustion fuels used in boiler, engines or gas turbines and resources in chemical industries. Some problems affecting its industrial utilization and recommendations are described as follows:

(1) Poor oil quality. Compared with heavy petroleum fuel oil, the bio-oils have several undesired properties for fuel applications such as high oxygen/water contents, high viscosity, and corrosiveness. These undesired properties present many obstacles to use bio-oil as a substitute for petroleum-based fuel.
(2) High upgrading cost. Over the years various technologies have been developed for bio-oil upgrading, including hydrotreating, hydrocracking, supercritical fluids extraction, solvent addition/esterification, emulsification, steam reforming, and chemical extraction. Solvent addition (esterification) appears to be the most practical approach due to simplicity, the low cost of some solvents and their beneficial effects on the oil properties. However, none of these bio-oil upgrading techniques has been commercialized due to low biofuel efficiency and their limitations.

(3) Novel integrated refinery processes are needed to systematically upgrade bio-oils into transportation fuels that have desirable qualities, while producing other value-added co-products to make the economics work.

Acknowledgment

The authors thank USDA-CSREES-Evans-Allen Project (NCX-238-5-09-130-1) for the financial support.

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